

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



Handwritten: Euro

(11)

EP 0 773 315 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
10.05.2000 Bulletin 2000/19

(51) Int Cl.7: **D04H 1/42, C08G 69/40**

(21) Application number: **96117688.0**

(22) Date of filing: **05.11.1996**

(54) **Nonwoven web comprising water soluble polyamides and articles constructed therefrom**

Wasserlösliche Polyamide enthaltende Faservliesen und daraus hergestellte Gegenstände

Nappe de non-tissé contenant du polyamide soluble dans l'eau et produits réalisés à partir de ces nappes

(84) Designated Contracting States:
DE FI FR GB IT SE

• **Van Lith, Greg J.**
Mounds View, Minnesota 55112 (US)

(30) Priority: **09.11.1995 US 555524**

(74) Representative: **Maiwald, Walter, Dr. Dipl.-Chem.**
Maiwald GmbH,
Elisenhof,
Elisenstrasse 3
80335 München (DE)

(43) Date of publication of application:
14.05.1997 Bulletin 1997/20

(73) Proprietor: **H.B. Fuller Licensing & Financing, Inc.**
St. Paul, Minnesota 55110-5132 (US)

(56) References cited:
EP-A- 0 176 316 **EP-A- 0 527 447**
US-A- 4 113 794 **US-A- 5 086 162**

(72) Inventors:
• **Ahmed, Sharf U.**
Woodbury, Minnesota 55125 (US)

EP 0 773 315 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**Field of the Invention**

5 [0001] This invention relates to a nonwoven web comprising a water soluble polyamide and articles constructed therefrom. The water soluble polyamide may be used alone or in combination with conventional thermoplastic web forming materials such as water insoluble polyethylene, polypropylene, polyester and polyamide. The water soluble polyamide may also be combined with biodegradable or selectively dispersible material to form nonwoven webs having various combinations of properties. Such water soluble webs have utility in the manufacture of disposable absorbent
 10 articles such as disposable diapers, feminine napkins, incontinent products and cellulosic articles such as tissues and towels, as well as for water soluble heat fusible webs for the textile industry.

Background of the Invention

15 [0002] Melt blown and spunbond webs typically comprise insoluble and nondegradable polymers such as water insoluble polyethylene, polypropylene, polyester and polyamide. Such webs are used in the manufacture of a variety of disposable products such as disposable diapers, feminine napkins, surgical gowns, laundry bags, bed pads, and the like. Such articles are designed to absorb and contain bodily fluids and/or provide a physical barrier to such fluids. Water soluble and biodegradable nonwoven webs may provide some solutions to environmental concerns regarding
 20 the disposal of such items.

[0003] Heat fusible webs are used for a variety of uses. In the textile industry, heat fusible webs are used to hold pieces of fabric, such as a patch pocket, in place prior to being sewn. These heat fusible webs are also used to create
 25 hems on pants or for a variety of ornamental craft appliques. Webs currently available for such uses are typically low viscosity at application temperature and insoluble in water. Upon activation with heat these materials often soak into the fabric workpiece causing the fabric to become stiff. Often the melted web soaks in to the extent that it fails to form the intended bond and reapplication is necessary.

[0004] A water soluble nonwoven comprising polyvinyl alcohol (PVOH) is taught in Dever et al., JP 59041260. Modifying the rate of water solubility of a PVOH based melt blown material using two different chemical treatments is described in the Development and Evaluation of Water Soluble Melt Blown Nonwovens, Dever, Benson, and Pair, INDA
 30 JNR, Vol. 5, No. 2, published 1993.

[0005] PVOH as a base polymer for the formation of a water soluble web suffers from several disadvantages. Due to its high melt point and poor thermal stability, it is very difficult to thermally process. An extruder, rather than merely a melt tank, is required to process the PVOH into a web. Additionally, once the web is formed, it has poor heat seal properties such that it would need to be heat scaled at temperatures that adversely affect the integrity of the substrate.

35 [0006] Water soluble polyamide prepared from adipic acid and polyoxyethylene diamine is reported by Fagerberg et al., U.S.A. Patent No. 3,882,090 and Speranza et al., U.S.A. Patent No's 5,086,162, 5,324,812 and 5,118,785. However, no such compositions have been used to form a water soluble nonwoven web or combined with other fibers
 40 to form nonwoven webs exhibiting a variety of properties.

[0007] The applicants have found that certain water soluble polyamides exhibit improved melting characteristics for manufacturing spunbond and melt blown nonwoven webs.

45 [0008] The European patent application EP-A-0 527 447 discloses a composition of matter comprising a blend of from 50 to 90 weight percent of a copolymer of a (meth)acrylate ester and (meth)acrylic acid, from 5 to 30 weight percent of a copolymer of ethylene and (meth)acrylic acid, or of a styrene/butadiene block copolymers and from 1 to 10 weight percent of a polyether block amide copolymer. In contrast to the present invention this teaching is directed to a polyamide which is not soluble in water.

Summary of the Invention

50 [0009] The present invention is a nonwoven web comprising a water soluble polyamide and articles constructed therefrom. The water soluble polyamide may be used alone or in combination with conventional thermoplastic web forming materials such as water insoluble polyethylene, polypropylene, polyester and polyamide. The water soluble polyamide may also be combined with biodegradable or selectively dispersible material to form nonwoven webs having various combinations of properties. The nonwoven web may be formed from spunbond and melt blown techniques as well as be sprayed molten or in an aqueous dispersion form.

55 [0010] Furthermore, the polyamide may be sprayed or dispersed in water to be used as a binder bonding fibers in air laid or wet laid processes. This aspect is particularly useful for improving the strength of cellulosic absorbent products such as tissues and towels.

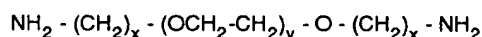
[0011] The resulting nonwoven can be used to form laminates such as those found in disposable articles to incor-

porate hydrophilic and water soluble features into the product. Such water sensitivity may facilitate recycling and composting efforts related to solid waste management as well as improve fluid transfer and acquisition. Additionally, non-woven webs comprising a water soluble polyamide are useful for making water soluble heat fusible webs. A 4,7,10 trioxatridecane-1,13-diamine is preferred due to its low melt temperature. Since the resulting web will dissolve during washing, such a web will overcome the problems of insoluble heat fusible webs used for temporary bonding in the textile industry.

Detailed Description of the Invention

[0012] The present invention is a nonwoven web comprising a water soluble polyamide. Such polyamides are taught by the above identified Fagerberg and Speranza patents and are produced by reacting at least one polyalkylene glycol diamine with at least one dicarboxylic acid or esters thereof.

[0013] The polyalkylene glycol diamine has the formula:



wherein X ranges from 2 to 3 and Y ranges from 1 to 2. Representative examples include triethylene glycol diamine, wherein X = 2 and Y = 1, and tetraethylene glycol diamine, wherein X = 2 and Y = 2. Commercial diamines of such include Jeffamine® 148 amine and Jeffamine® 192 amine. The preferred diamine is 4,7,10 - trioxatridecane-1,13-diamine (TTD diamine) wherein X = 3 and Y = 2.

[0014] Suitable dicarboxylic acids are those having from 5 to 36 carbon atoms including adipic acid, pimelic acid, azelaic acid, sebacic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, t-butyl isophthalic acid, dimer acid and mixtures thereof. The esters and anhydrides of these acids may also be used. Adipic acid is preferred.

[0015] The resulting water soluble polyether amide preferably has a melt point about 190°C or less as the case when adipic acid is reacted with Jeffamine® 148. More preferably, the melt point is about 155°C or less as the case when adipic acid is reacted with Jeffamine® 192. The most preferred water soluble polyether amide has a melt point about 150°C or less as the case when adipic acid is reacted with TTD diamine. This particular combination results in a faster setting, strong, easily processed water soluble polyether amide. The low melt temperature makes this combination particularly preferred for heat fusible webs. Often heat fusing such webs at temperatures above 150°C adversely affects the integrity of the substrates to be bonded. The resulting web is insoluble in dry cleaning solvent rendering the article (fabric) dry cleanable when necessary.

[0016] The resulting polyamide may be formed into a web by means of known melt blown or spunbond techniques. Alternatively, the polyamide may be sprayed molten or as an aqueous dispersion during other nonwoven manufacturing processes such as air laid or wet laid processes to bind fibers and impart strength.

[0017] The polyamide may be used alone or in combination with other polymers to create a variety of useful properties in the resulting web. By combining the water soluble polyamide with conventional insoluble polymers such as polyethylene, polypropylene, polyester or polyamide sequentially during the web forming process, the resulting web will have a water soluble matrix. Preferably, the insoluble polymer is applied to form a discontinuous web. The water soluble polyamide is then applied to the discontinuous regions such that the resulting web dissolves at the locations of the polyamide leaving small portions of the insoluble portions intact. Alternatively, the water soluble polyamide may be applied as a continuous phase with discontinuous regions of the insoluble polymer. This technique creates a low cost flushable web. By combining the water soluble polyamide with at least one insoluble polymer simultaneously, it is possible to create webs having hydrophilic character that do not disperse in water.

[0018] The polyamide may additionally be combined with biodegradable materials or selectively dispersible materials to create nonwoven webs having unique combinations of properties. As in the case of the more conventional polymers, depending on the method, sequences and ratios by which they were combined, the web may or may not be water dispersible. If the polyamide is added sequentially during the web forming process, each material tends to maintain its unblended properties, whereas simultaneously combining the polyamide in the melt phase with at least one other polymer results in webs with properties intermediate between the unblended polymers. The polymer present at the higher concentration tends to govern the overall properties of the nonwoven web.

[0019] Useful biodegradable polymers include those which are photodegradable, microbiologically and hydrolytically degradable, as well as cellulose so long as the polymer can be incorporated into a web either alone or combined with a compatible carrier. Representative Examples include polylactic acid, polyhydroxybutyrate, polyhydroxybutyrate-valerate, polycaprolactone, and mixtures thereof.

[0020] Selectively dispersible polymers include those which are dispersible in aqueous environment under prescribed conditions, yet are not dispersible in all aqueous environments. Examples include materials that are alkaline dispersible or saline insoluble. The Eastman AQ copolyesters, which are water dispersible yet saline insoluble are preferred for

articles intended to absorb body fluids.

EXAMPLES

Example 1:

[0021] A water soluble polyamide was produced by reacting adipic acid with TTD diamine such that the resulting polyamide had a viscosity of about 10,000 cps to about 12,000 cps at 400°F as measured by a Brookfield viscometer. Preferably, stearic acid is utilized at concentrations of about .5-2% to control the viscosity. Reaction conditions are maintained at a temperature of about 400°F or as low as possible to insure the resulting polyamide is light in color. The polyamide was sprayed with a Bayer and Otto hotmelt spray gun to form a nonwoven web. The polyamide was premelted at 400°F in an oven and sprayed onto release paper while maintaining an application temperature ranging from about 390°F to 400°F. At a pressure of about 40psi, the basis weight of the web was 72.5 g/m² whereas at a pressure of 60psi the basis weight was reduced to 33.9 g/m². The applicants surmise that nonwoven web may be formed with commercial meltdown or spunbond web forming equipment at temperatures ranging from about 375°F to 400°F. The polyamide was also used to form a nonwoven web with J & M meltblown hot melt spray applicators at a temperature of 400°F. Both webs were readily soluble in tap water such that a 1" x 1" piece will solubilize in approximately 20 minutes without agitation.

Example 2:

[0022] A second polyamide was produced from the same reactants as Example 1 without stearic acid such that the viscosity is about 35,000 cps at 400°F. The polyamide was sprayed with a Bayer and Otto hotmelt spray gun at a temperature of about 400°F. The basis weight can be adjusted with the air pressure as in Example 1. The resulting nonwoven web resembled conventional spunbond nonwoven formed from water insoluble polyester or polypropylene, yet the web is readily soluble in tap water.

Example 3:

[0023] The polyamide of Example 2 was combined with a compatible water insoluble polyamide produced by reacting primarily dimer acid with ethylene diamine such that the viscosity of the water insoluble polyamide was about 58,000 cps at 400°F. The polyamides were melted and combined at a ratio of 4 parts water soluble polyamide to 1 part insoluble polyamide and at a ratio of 1 part water soluble polyamide to 4 parts water insoluble polyamide. The blended polyamides were then sprayed with a Bayer and Otto spray gun at a temperature ranging from about 410°F to 420°F to form a web resembling conventional meltblown or spunbond nonwoven. The web formed from 4 parts water soluble polyamide readily disperses in tap water. The web formed from 1 part water soluble polyamide is not dispersible in water, yet is hydrophilic. Therefore, blends of small concentrations of water soluble polymers with insoluble polymers are useful for imparting hydrophilicity into nonwoven webs. This is particularly useful for creating hydrophilic zones in line for disposable absorbent products.

Example 4:

[0024] An Eastman AQ copolyester having an intrinsic viscosity of about .2 was sprayed on both sides of the water soluble web formed in Example 1. The Eastman AQ copolyesters are soluble in water, yet saline or body fluid insoluble. The resulting web disperses in water yet is not dispersible upon submersion in saline for 45 minutes.

Example 5:

[0025] The water soluble polyamide of Example 1 was sprayed simultaneously with an experimental biodegradable polymer, Eastman Polyester 14766, to form a fused nonwoven web. Upon placing the web in water, some dissolution was observed yet the web remained intact due to the presence of the polyester. This combination is particularly preferred for disposable diapers as a possible solution for solid waste management concerns. When the water soluble polyamide was combined with the Eastman Polyester 14766 sequentially, the discreet webs could be easily separated from each other. Applicants surmise the polyamide could be sprayed simultaneously with any water insoluble polymer that is suitable for web forming processes.

Example 6:

[0026] The water soluble webs of Examples 1 and 2 are heat fusible. Examples 3-5 may also be heat fusible, but will no longer be 100% soluble. In order to compare the properties of the improved water soluble web of the present invention, it was compared to PVOH. Although nonwoven web comprising PVOH are known, such webs are not commercially available. Applicants attempted to create a nonwoven web with hot melt spray applications as in Examples 1-5.

[0027] Vinex 2019, PVOH commercially available from Air Products was heated at 170°C. After 30 minutes the Vinex 2019 had turned light brown due to degradation. Since the material was unflowable at 170°C, the temperature was increased to about 210°C upon which the Vinex 2019 turned very dark in appearance and fumed. Therefore, such attempts were unsuccessful due to the poor thermal stability and processability to PVOH.

[0028] Since a nonwoven web could not be formed from PVOH without the extrusion meltblown equipment taught by Dever, Benson and Pair in the INDA publication mentioned above, the applicants formed a film from an aqueous emulsion to compare the heat seal properties. A 15% aqueous solution of Vinex 2019 and a 15% aqueous solution of the water soluble polyamide of Example 1 were used to cast films. Upon drying, the thickness of the resulting films was about 1 to 2 mils.

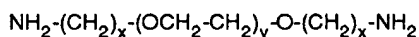
[0029] The films were cut into pieces and used to heat seal standard copy paper with a small iron. Table 1 depicts the results of the heat seal bonds and this demonstrates the improved properties of the water soluble polyamide with respect to PVOH.

TABLE 1

Temperature	Time	Result
290-305°F 143°C - 152°C	1 Minute	Vinex 2019 Did not bond the paper. It stuck to the side which was pressed by iron but peeled off easily when cooled. No fiber tear.
290-305°F 143°C - 152°C	1 Minute or 30 Seconds	Example 1 Gave excellent bond. Gave fiber tear.
390-410°F 199 - 210°C	1 Minute	Vinex 2019 Only bonded to the paper side which was directly in contact with iron, but did not bond paper on both sides.
390-410°F 199 - 210°C	30 Seconds	Example 1 gave excellent bonds and fiber tear.

Claims

1. A nonwoven web comprising a water soluble polyether amide produced by reacting at least one polyalkylene glycol diamine with at least one decarboxylic acid or esters thereof, said polyalkylene glycol diamine having the formula:



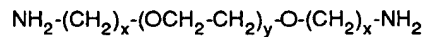
wherein x ranges from 2 to 3 and y ranges from 1 to 2; wherein said web is produced by the use of spunbond techniques or melt blown techniques, or by spraying water soluble polyether amide in molten or in an aqueous dispersion form.

2. The nonwoven web of claim 1, wherein at least one of said polyalkylene glycol diamines is 4,7,10-trioxatridecane-1,13-diamine.
3. The nonwoven web of claim 1, further comprising at least one polymer selected from the group consisting of a biodegradable polymer, a water insoluble polymer and a selectively dispersible polymer.
4. The nonwoven web of claim 3, wherein said biodegradable polymer is selected from the group consisting of polylactic acid, polyhydroxybutyrate, polyhydroxybutyrate-valerate, polycaprolactone, and mixtures thereof.
5. The nonwoven web of claim 3, wherein the water insoluble polymer is selected from the group consisting of polyethylene, polypropylene, polyester, polyamide and mixtures thereof.
6. The nonwoven web of claim 1, wherein said web is heat fusible.

7. A disposable adsorbent article comprising the nonwoven web of claim 1, 4 and 6.
8. The article of claim 7, wherein said article is selected from the group consisting of disposable diapers, feminine napkins, surgical gowns, bed pads, and the like.
9. A flushable, disposable article comprising a nonwoven web of claims 1 to 6 having portions of at least one water soluble polyamide and portions of a water insoluble polymer in contact with each other.
10. The flushable, disposable article of claim 9, wherein said water soluble polyamide portions form a continuous matrix.
11. The flushable, disposable article of claim 9, wherein said water soluble polyamide portions substantially surround said water insoluble polymer portions.

Patentansprüche

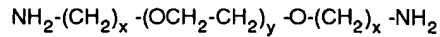
1. Faservlies, umfassend ein wasserlösliches Polyetheramid, hergestellt durch Umsetzen von mindestens einem Polyalkylenglycoldiamin mit mindestens einer Dicarbonsäure oder Estern davon, wobei das Polyalkylenglycoldiamin die Formel hat:



- worin x zwischen 2 und 3 liegt und y zwischen 1 und 2 liegt; wobei das Vlies unter Verwendung von Schmelzspinn- oder Schmelzblastechniken oder durch Sprühen von wasserlöslichem Polyetheramid in geschmolzener Form oder in Form einer wässrigen Dispersion hergestellt wird.
2. Das Faservlies nach Anspruch 1, worin mindestens eines der Polyalkylenglycoldiamine 4,7,10-Trioxatridecan-1,13-diamin ist.
3. Das Faservlies nach Anspruch 1, weiter umfassend mindestens ein Polymer, ausgewählt aus der Gruppe, bestehend aus einem bioabbaubaren Polymer, einem wasserunlöslichen Polymer und einem selektiv dispergierbaren Polymer.
4. Das Faservlies nach Anspruch 3, worin das bioabbaubare Polymer ausgewählt ist aus der Gruppe, bestehend aus Polymilchsäure, Polyhydroxybutyrat, Polyhydroxybutyrat-Valerat, Polycaprolacton und Gemischen davon.
5. Das Faservlies nach Anspruch 3, worin das wasserunlösliche Polymer ausgewählt ist aus der Gruppe, bestehend aus Polyethylen, Polypropylen, Polyester, Polyamid und Gemischen davon.
6. Das Faservlies nach Anspruch 1, worin das Vlies wärmeschmelzbar ist.
7. Ein Einwegadsorbtiionsartikel, umfassend das Faservlies nach Anspruch 1, 4 oder 6.
8. Der Artikel nach Anspruch 7, worin der Artikel ausgewählt ist aus der Gruppe bestehend aus Wegwerfwindeln, Damenbinden, OP-Kleidung, Bettpolster und ähnlichem.
9. Ein auswaschbarer Einwegartikel, umfassend ein Faservlies nach einem der Ansprüche 1 bis 6 mit Anteilen von mindestens einem wasserlöslichen Polyamid und Anteilen eines wasserunlöslichen Polymers in Kontakt miteinander.
10. Der auswaschbare Einwegartikel nach Anspruch 9, worin die wasserlöslichen Polyamidanteile eine kontinuierliche Matrix bilden.
11. Der auswaschbare Einwegartikel nach Anspruch 9, worin die wasserlöslichen Polyamidanteile im wesentlichen die wasserunlöslichen Polymeranteile umgeben.

Revendications

1. Tissus non-tissé (« nonwoven web ») comprenant un polyether amide produit par la réaction d'au moins une polyalkylène glycol diamine avec au moins un acide décarboxylique ou des esters de ceux-ci, ledit polyalkylène glycol diamine présentant la formule :



- caractérisé en ce que x est de l'ordre de 2 à 3 et y est de l'ordre de 1 à 2 ; caractérisé en ce que ledit tissu est produit en utilisant les techniques du type tissu non tissé (« spunbond techniques ») ou des techniques de soufflage fondu (« melt blown techniques »), ou en aspergeant le polyether amide qui est soluble dans l'eau sous une forme fondue ou sous forme de dispersion aqueuse.

2. Tissu non-tissé selon la revendication 1, caractérisé en ce que au moins une des polyalkylène glycol diamines est la 4, 7, 10-trioxatridecane-1,13-diamine.

3. Tissu non-tissé selon la revendication 1, caractérisé en ce qu'il comprend en outre au moins un polymère sélectionné à partir du groupe consistant en un polymère biodégradable, un polymère insoluble dans l'eau et un polymère dispersible sélectivement.

4. Tissu non-tissé selon la revendication 3, caractérisé en ce que ledit polymère biodégradable est sélectionné à partir du groupe consistant en un polymère biodégradable en un acide polylactique, le polyhydroxybutyrate, le polyhydroxybutyrate-valeate, la polycaprolactone, et des mélanges de ceux-ci.

5. Tissu non-tissé selon la revendication 3, caractérisé en ce que le polymère insoluble à l'eau est sélectionné à partir du groupe consistant en le polyéthylène, le polypropylène, le polyester, le polyamide et un mélange de ceux-ci.

6. Tissu non-tissé selon la revendication 1, caractérisé en ce que ledit tissu est fusible à la chaleur (« heat fusable »).

7. Article adsorbant jetable comprenant le réseau non-tissé de la revendication 1, 4 et 6.

8. Article adsorbant jetable selon la revendication 7, caractérisé en ce que ledit article est sélectionné à partir du groupe consistant en des couches de bébé, des serviettes hygiéniques, des blouses de chirurgie, des coussins de lit (« bed pads ») et analogues.

9. Article jetable que l'on peut rincer comprenant un réseau non tissé selon les revendications 1 à 6 présentant des portions d'au moins un polyamide soluble à l'eau et des portions d'un polymère insoluble dans l'eau en contact les unes avec les autres.

10. Article jetable que l'on peut rincer selon la revendication 9, caractérisé en ce que lesdites portions de polyamide soluble forment une matrice continue.

11. Article jetable que l'on peut rincer selon la revendication 9, caractérisé en ce que lesdites fractions de polyamide solubles à l'eau entourent sensiblement lesdites portions de polymère insolubles à l'eau.